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# Mössbauer Spectroscopy, X-Ray Diffraction and SEM Studies on Multiferroic $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ Ceramics

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Magnetoelectric multiferroics are materials which exhibit both magnetic order and ferroelectricity in the same phase. Multiferroic materials, where ferroelectricity and magnetism coexist, were extensively studied. This class of materials offers a large application potential for new devices due to the two coupled degrees of freedom based on the local off-centered distortion and the electron spin. The studied  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics was prepared by conventional synthesis and hot uniaxial pressing reaction applying the conventional mixture of  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3$  oxides as precursor materials. The present work focuses on the structure analysis of multiferroic  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics performed by X-ray diffraction method, scanning electron microscopy and the Mössbauer spectroscopy methods.

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## 1. Introduction

The  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  (BTF) multiferroic ceramics is used for construction of different types of memory elements like a shape or information [1]. This ceramic material belongs to ferroelectromagnetics and is characterized by presence of simultaneous magnetic and ferroelectric ordering [2–6]. The term of a multiferroic was introduced by Schmid in 1994 and it describes materials showing at least two ferroic states simultaneously in the same phase. In the multiferroic materials  $M_s$  (the parameter of the magnetic system ordering),  $P_s$  (the parameter of the electric system ordering) and  $\eta_s P_s$  (the parameter of the elastic-magnetic system ordering) can be changed by both magnetic field ( $H$ ), electric field ( $E$ ) and by mechanical stress ( $\sigma$ ) [8–10].

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Majority of ferroelectromagnetics have a layer perovskite-like structure. Structures of this type were discovered for the first time by Aurivillius in 1949 [2] and Subbaro described them in 1969 by a general formula in the form of

$$A_{m-1}Bi_2B_mO_{3m+3}, \quad (1)$$

where big cations A are:  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Bi^{3+}$ ,  $Pb^{4+}$ , whereas B ones are cations of transient metals:  $Ti^{4+}$ ,  $Nb^{5+}$ ,  $Ta^{5+}$ ,  $Mo^{6+}$ ,  $W^{6+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ , and  $m$  designates the number of perovskite layers along the thickness ( $m = 1, 2, 3, 4, 5, 8$ ) [6–14]. This means that the layers are composed of chains of oxygen octahedrons with thickness  $m$  separated by bismuth–oxygen layers interleave with each other.

By introducing  $Fe^{3+}$  cations into place B a group of compounds called ferroelectromagnetics can be obtained with a general formula

$$Bi_4Bi_{m-3}Ti_3Fe_{m-3}O_{3m+3}. \quad (2)$$

The  $Bi_5Ti_3FeO_{15}$  ceramics can be regarded as model of this type of ferroelectromagnetics.

The aim of this work was to develop the technology of biferroic  $Bi_5Ti_3FeO_{15}$  ceramics preparation exhibiting a layer perovskite-like structure of the type according to formula (2) where  $m = 4$ , and with its characteristic microstructure and dielectric properties. Structure data for studied ceramics were obtained by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) methods whereas hyperfine parameters were obtained from the Mössbauer spectroscopy (MS) studies.

## 2. Experimental details

The course of the synthesis of complex oxides using the mixture of simple oxides as precursor materials depends mainly on the dispersion degree of the charge, its homogeneity, temperature and time of sintering.

The tested material was prepared in two stages. In the first stage it was obtained as a result of the reaction in the solid phase synthesis from the refined pressed mixture of the  $Bi_2O_3$ ,  $TiO_2$  and  $Fe_2O_3$  simple oxides following the reaction:



The synthesis reaction was conducted at  $800^\circ C$  for 5 h by the method of free sintering. The synthesized powder was subjected to pressing giving discs of 10 mm in diameter. The second stage of the technology was the free sintering process conducted twice for 5 h at  $1040^\circ C$  to obtain the desired material.

X-ray diffraction pattern was collected by X-Pert Philips diffractometer equipped with curved graphite monochromator on diffracted beam and with following slits (in the sequence from copper tube to proportional counter): Soller ( $2^\circ$ ), divergence ( $1/2^\circ$ ), antiscatter ( $1/2^\circ$ ), Soller ( $2^\circ$ ) and receiving (0.15 mm). The data of diffraction lines were recorded by the “step-scanning” method in  $2\theta$  range from  $10^\circ$  to  $140^\circ$  and  $0.05^\circ$  step.

The SEM (HITACHI S-4700 NORAN Vantage) method and energy dispersion spectroscopy (EDS) technique were applied for the analysis of the morphology

of ceramic samples and their chemical composition, respectively. The measurements of the  $^{57}\text{Fe}$  Mössbauer spectra were performed in transmission geometry by means of a constant spectrometer of standard design and with a conversion electron Mössbauer spectroscopy technique. The 14.4 keV gamma rays were provided by a 50 mCi source of  $^{57}\text{Co}/\text{Rh}$ . The spectra of the samples were measured at room temperature. Hyperfine parameters of the investigated spectra were related to the  $\alpha\text{-Fe}$  standard.

### 3. Results

Figure 1 shows the SEM images of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics compacted by the method of free sintering. These images reveal lamellar grains of different orientation, overlapping one another. The thickness of lamellae is quite similar and equals to about  $1\ \mu\text{m}$  whereas their diameter size distribution is rather broad. Such morphology is characteristic of layer structures of the Aurivillius type.

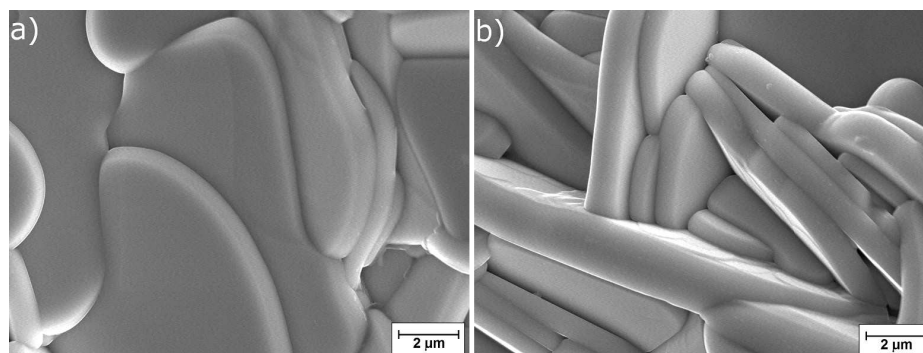


Fig. 1. SEM images of fractures of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics.

The X-ray diffraction analysis revealed that the sample obtained by the free sintering method contains a single  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  (ICDD PDF 82-0063) ceramic phase (Fig. 2).

The  $^{57}\text{Fe}$  Mössbauer spectra were applied to the analysis of the local environment of the iron atoms in the studied  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase. The Mössbauer spectra obtained in transmission (TS) and by conversion electron Mössbauer spectroscopy (CEMS) collected at room temperature are shown in Figs. 3 and 4, respectively.

The best fit for the experimental data was obtained with the use of two quadrupole doublets; hyperfine parameters are presented in Table. The application of two subspectra show the presence of two Fe sites in the structure. The relative areas of two doublets are equal to 63% and 37%, respectively, and indicate that the sites are approximately equally occupied. In the investigations by CEMS the samples were prepared as pellets.

In the Mössbauer spectra the size of the isomer shifts are the result of both the coordination and valence of the iron in the material under investigation. The

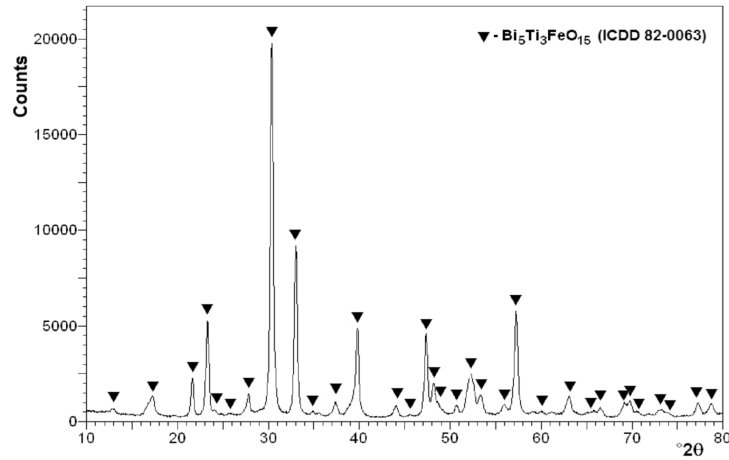


Fig. 2. X-ray diffraction pattern of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics.

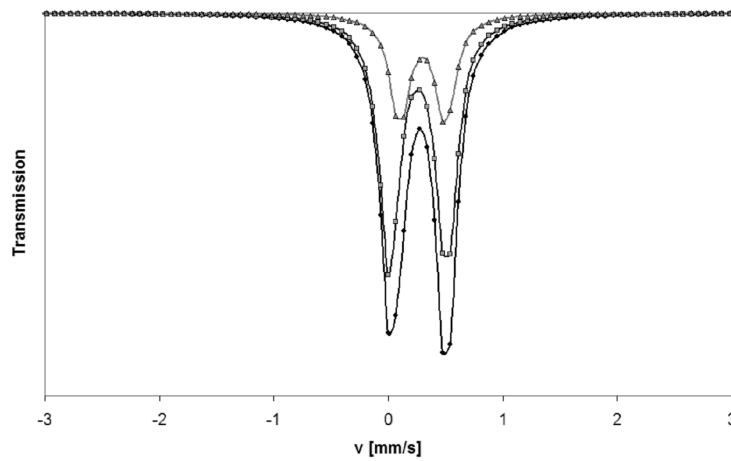
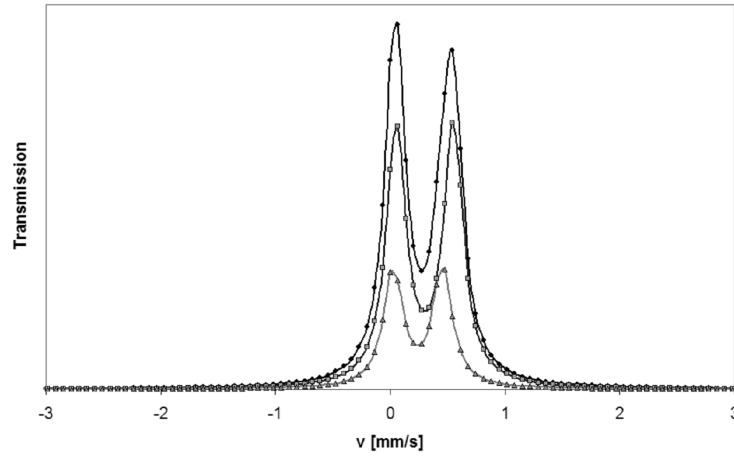


Fig. 3. Transmission Mössbauer spectrum for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics.

quadrupole splitting arises from the interaction between the nuclear quadrupole moment and a non-zero electric field gradient at the nucleus. The size of the quadrupole splitting is determined by valence electrons and ligands and therefore provides information on the oxidation state, coordination number, and site distortion. Values of  $\text{IS} = 0.25 \text{ mm/s}$  and  $\text{QS} = 0.45 \text{ mm/s}$  are typical of  $\text{Fe}^{3+}$  ions in an octahedral environment [15–17]. Therefore, we can conclude that in  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase there are two iron sites, both occupied by  $\text{Fe}^{3+}$  and surrounded by a distorted octahedron of oxygen atoms with different degrees of distortion.

Fig. 4. Conversion electron Mössbauer spectrum for  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics.

TABLE

Hyperfine parameters of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  sample.

	Subspectra	IS [mm/s] $\pm 0.005$ mm/s	QS [mm/s] $\pm 0.005$ mm/s	A [%] $\pm 2\%$
$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (TS)	Q-1	0.27	0.49	63
	Q-2	0.26	0.42	37
$\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (CEMS)	Q-1	0.23	0.40	72
	Q-2	0.31	0.45	28

Relative to  $\alpha$ -Fe foil at room temperature.

#### 4. Conclusions

- Synthesis by the free sintering process enabled us to obtain a single phase multiferroic  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics.
- The Mössbauer studies performed by CEMS technique confirmed that the studied ceramic material contains only one phase —  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ .
- Analysis of hyperfine parameters points to the presence of  $\text{Fe}^{3+}$  ions in two different oxygen environments.
- The Mössbauer spectroscopy confirmed the magnetic properties and homogeneous atom distribution.

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